

Trace Metal Analysis of Agricultural Salt Products

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ABSTRACT

The analysis of a wide assortment of materials for traces and larger amounts of a great many metals is now routinely accomplished by the atomic absorption spectrophotometric (AAS) technique. This paper describes the AAS determination of six mineral nutrients in agricultural salt products. It discusses the selection of sample sizes for products containing calcium, cobalt, copper, iron, manganese, and zinc, usually in the range of 0.01% (Co) to 2.0% (Ca); the preparation of samples for analysis by AAS; and the concentrations of sample solutions most convenient for analysis. It outlines the choice of instrument operating conditions and parameters, and considers some of the means for overcoming interferences.

INTRODUCTION

The atomic absorption technique is approaching the end of its second decade of application to analytical uses. The problems and advantages of the technique are well catalogued, and this paper will not dwell on the savings in time and the often greater analytical sensitivities which this technique provides as compared to other, classical methods. The literature abounds in reports of the research into the uses and technical refinements of atomic absorption spectrophotometry (AAS). Though there are numerous papers on the determination of traces of metals in water and brines, relatively little has been published on the analysis of salt by AAS. Of particular interest is a paper presented at the last salt symposium (Lynch, 1970). Also of much interest is the informal report on the Atomic Absorption Seminar organized by the Salt Institute and held in October, 1970 (Fiedelman, 1970).

Texas Brine Corporation's Research & Development Laboratory was recently assigned the task of developing an in-house quality control program for United Salt Cor-

poration's line of mineralized agricultural salt products. The availability of the laboratory's atomic absorption spectrophotometer, and the high level to which the AAS technique has advanced in the past decade, dictated the method of analysis to be applied. The procedures and methods were developed primarily for the analysis of mineralized salt, but with little modification are applicable to the analysis of mineral premixes as well.

The composition of a typical salt product is outlined in Figure 1. In addition to the elements listed, calcium is a constituent of this product and normally is present at a level of several per cent in products of this type. The metals of interest in the analysis of agricultural salt products—calcium, cobalt, copper, iron, manganese, and zinc—actually are present in the salt in amounts greater than those normally labelled by the chemist as "trace." That is, they are at or above the 100 ppm (or 0.01%) level in the salt. Thus the problem in mineralized salt analysis is not one in which the ultimate in sensitivities and detection limits is essential. Rather, it is one of handling relatively high concentrations of the six metals in a difficult matrix. Our approach to this problem is dictated by the fact that we are interested primarily in demonstrating to the customer that the minimum guaranteed amounts of the metals are indeed to be found in the salt.

SAMPLE PREPARATION

Prior to analysis by atomic absorption, the salt samples must be suitably prepared. While salt prior to mineralization will require little preparation for analysis, mineral additives complicate the matter considerably. The size of the sample to be analyzed depends largely on the amounts of minerals added to the particular salt mix. Since in all cases we are dealing with greater than trace level amounts, samples may be dissolved and suitably diluted to bring the

NET WEIGHT SHOWN ON BAG	
GUARANTEED ANALYSIS	
Salt (NaCl), not more than	95.0 %
Salt (NaCl), not less than	91.0 %
Manganese (Mn), not less than	0.30 %
Zinc (Zn), not less than	0.25 %
Iron (Fe), not less than	0.15 %
Copper (Cu), not less than	0.015 %
Cobalt (Co), not less than	0.01 %
Iodine (I), not less than	0.01 %
MANUFACTURED BY	
UNITED SALT CORPORATION	
HOUSTON, TEXAS	

Figure 1. United Trace Mineralized Salt: Guaranteed Analysis.

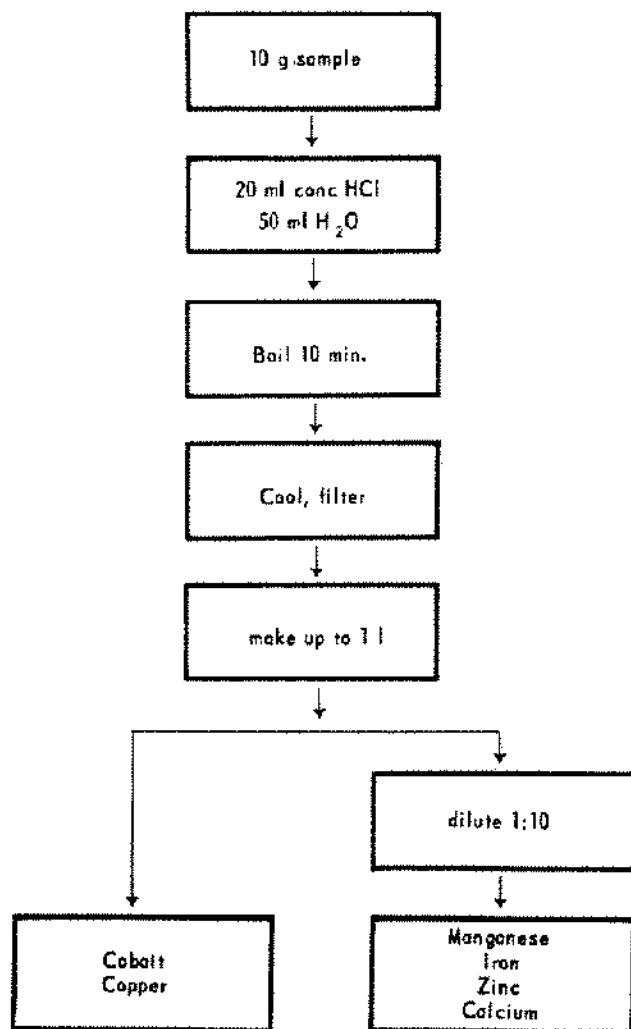


Figure 2. Analytical Flow Sheet.

concentrations of the metals of interest into a convenient range for analysis. Figure 2 outlines our procedure.

Sample size

The degree of dilution is governed by two factors: first, the detection limits constrain us from diluting beyond a certain level; and second, the levels of solids tolerated by the nebulizer tube and burner head demand some minimal dilution. Due to interferences from high solids salt matrices, solutions of more than a few per cent should be avoided; we prefer to deal with solids in the vicinity of 0.1%.

Figure 3 simplifies the selection of proper sample sizes for the particular type of salt being analyzed. It correlates sample size with the amounts of metals in the dry salt and in solution, over the metals' analytical ranges. From this diagram and the guaranteed analysis (Figure 1), we may easily determine the sample size required. Iron, for instance, is guaranteed to be not less than 0.15%, and the useful analytical range for iron is up to approximately 20 ppm. Therefore, the sample size should be restricted to no more than about 7 grams per liter for determinations of iron. Salt samples are conveniently 10 grams per liter, and dilutions of 1:10 (which satisfies the sample size requirement for iron) and even 1:100 of this solution are required for the higher concentration constituents, particularly calcium. The 10- and 100-fold dilutions, of course, satisfy the desire for low solids matrices.

Dissolution

Two factors complicate the second step in sample preparation, dissolution of the sample. First, all of the mineral additives, unlike the salt, are insoluble in water. Second, organics are present in the salt as nutrients and binders. For total dissolution of all the minerals, it is necessary to use appropriate mineral acids and to heat the sample. Sulfuric and phosphoric acids cannot be used because they lower calcium recovery through the formation of insoluble, refractory calcium salts of those acids. Use of cold acids drastically reduces the recovery of iron, and of manganese to a lesser extent. Furthermore, the destruction of organics, largely molasses and mineral oil, also require that samples be heated to boiling. Therefore, samples are boiled in concentrated acid, either hydrochloric or nitric, on a magnetic stirrer-hot plate in a fume hood. Additional distilled water is added, and the solution is further stirred to ensure complete dissolution of both mineral additives and salt.

Filtration and dilution

After the sample has been dissolved, it must be filtered to eliminate particulate matter and organics which might plug the nebulizer capillary or lead to light scattering in the flame. Current practice is to vacuum filter through filters whose pore sizes range down to 0.45 microns.

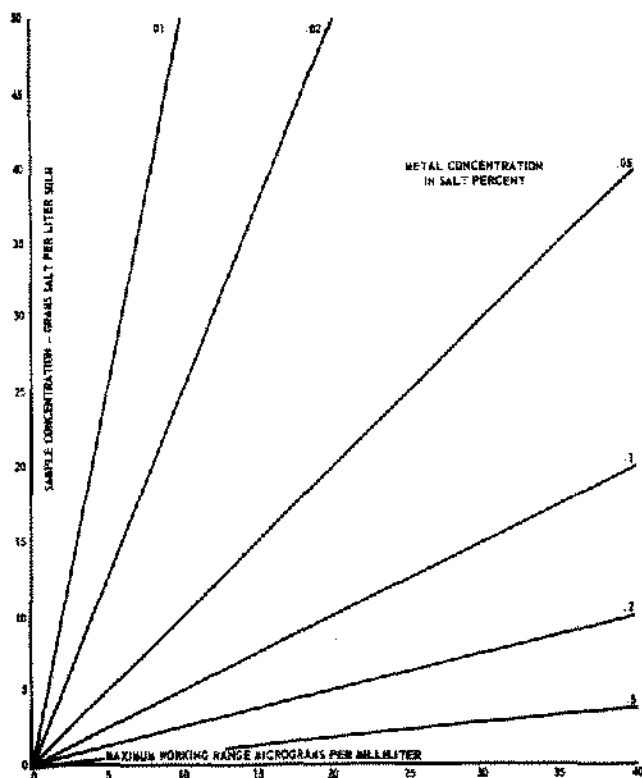


Figure 3. Salt Sample Size for Various Metals.

The filtration step is the most tedious since several filtrations are required. Filtration time is extended to an inordinate degree if the samples are not sufficiently boiled. (The destruction of organics is more effectively accomplished by boiling the sample in nitric acid until the evolution of red fumes, followed by boiling with perchloric acid. Filtration should be easier following this procedure. However, it requires a perchloric acid fume hood, which we lack).

Filtered samples are diluted to 1000 milliliters with distilled water. The resulting concentrations of both salt and acid are approximately one per cent. Dilutions of 10- and 100-fold are made up with dilute (1% v/v) acid.

INSTRUMENTAL

Equipment

All analyses were performed on a Perkin-Elmer Model 403 double beam spectrophotometer. Read-out is digital in either absorbance or concentration, and these values are recorded on a strip chart recorder for permanent record. Spectral lines for the six metals were provided by Perkin-Elmer single element hollow cathode lamps. Figure 4 lists the monochromator and lamp settings recommended by the manufacturer, and used in our work.

A three-slot burner head is employed, since it allows

Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer	Calcium	Cobalt	Copper	Iron	Manganese	Zinc
P/E Hollow Cathode Tube Type	303-6012 M2379	303-6022 M2504	303-6024 M2230	303-6037 M2148	303-6043 M2456	303-6081 M1260
Filament Current milliamperes	10-25	30-40	15-25	30	20-30	15-20
Slit Number	4	3	4	3	3	4
Spectral Bandwidth nanometers	1.4	.2	.7	.2	.2	.7
Filter	VIS	UV	UV	UV	UV	UV
Wave Length nanometers	422.7	240.7	324.7	248.3	279.5	213.9
Working Range micrograms milliliter	40	20	20	20	10	5

Figure 4. Operating Parameters.

Flame	Gas Flow Rates				Gas Pressures			
	Flowmeter Setting		Liters / Minute		Cylinder Head		Control Box	
	C ₂ H ₂	Air	C ₂ H ₂	Air	C ₂ H ₂	Air	C ₂ H ₂	Air
Slightly fuel-rich ^a	45	70	5.5	27.8	12	40-100	8	30
Very fuel-rich	37	50	4.3	19.6	12	60	8	30

^a Manufacturer's recommendations. (Perkin-Elmer, 1973, General Information, pp. 11-12)

Figure 5. Gas Pressures and Flow Rates.

relatively high solids solutions to be burned for longer periods of time than the conventional burner head before cleaning becomes necessary. It also produces a wider flame, which intersects a greater portion of the source beam and thereby results in greater absorbances by atomized species. Newer versions of the 3-slot burner are made of titanium rather than stainless steel, which permits aspiration of highly acidic solutions without interference from flame contamination consequent to burner head corrosion.

Flame parameters

The flame is air-acetylene. The manufacturer recommends the use of a "slightly yellow, fuel-rich flame". (Perkin-Elmer, 1972) We have found that reducing the air flow below that recommended by the manufacturer results in a flame which gives greater absorbances. Reducing the air flow produces a very yellow, luminescent flame which is highly reducing, compared to the bluish, nearly stoichiometric flame produced at the recommended settings (See Figure 5).

For both the nearly stoichiometric (bluish) and fuel-rich (incandescent) flames, the maximum absorbances are observed at or near the base of the flame. Varying the fuel/air ratios from the optimum (4.3 liters acetylene/minute, 19.6 liters air/minute) does not result in greater net absorbances, for increasing the fuel/air ratio further will produce a more luminous flame which absorbs across a broad range of the spectrum. The optimum, highly luminous flame will produce some soot, but such cleaning of the burner head as is normally required for high solids matrices will be sufficient.

Maximization of absorbances requires two other adjustments, in nebulization rates and burner head alignment. Nebulization, or aspiration, rate adjustments may cause a change in the overall air flow rate, and after nebulization has been optimized the air flow should be checked. The burner head should be adjusted vertically to a point

just below the source beam, and horizontally. However, one of the advantages of the 3-slot burner head is that the absorption signal is less sensitive to burner head alignment along the axis of the light path, due to the flame's greater width.

WORKING CURVES

Working curves

In discussing sample sizes, reference was made to a "convenient analytical range." This is the range over which the working curve, constructed by plotting standard solution concentrations against their absorbances, is linear or nearly linear. Beyond this range, small uncertainties in absorbance readings lead to larger and larger uncertainties in concentration. When a high degree of precision is desired, a more constraining limitation is imposed, namely that concentrations should be selected such that the corresponding absorbances fall within the interval of 0.1 to 0.5 absorbance units. (Slavin, 1968, page 67) Figure 6 shows the working curves for the six metals of interest, and the linear working ranges of each. The useful analytical ranges are those cited in Figure 4; they govern the selection of dilution factors for samples, as shown in Figure 3.

Standards

All standards are made up from commercially available 1000 ug/ml single element standard reference solutions. It is convenient to make up composite standard solutions containing 100 ul/ml of each of the six metals by dilution of the 1000 ug/ml standards with dilute (1% v/v) acid. Stored in polyethylene bottles, these standards will last a considerable length of time. Standards which span the working ranges of the metals are made up by dilution with dilute acid of the composite 100 ug/ml standards. Time stability for these low concentration standards, also stored in polyethylene bottles, is less than that of the more con-

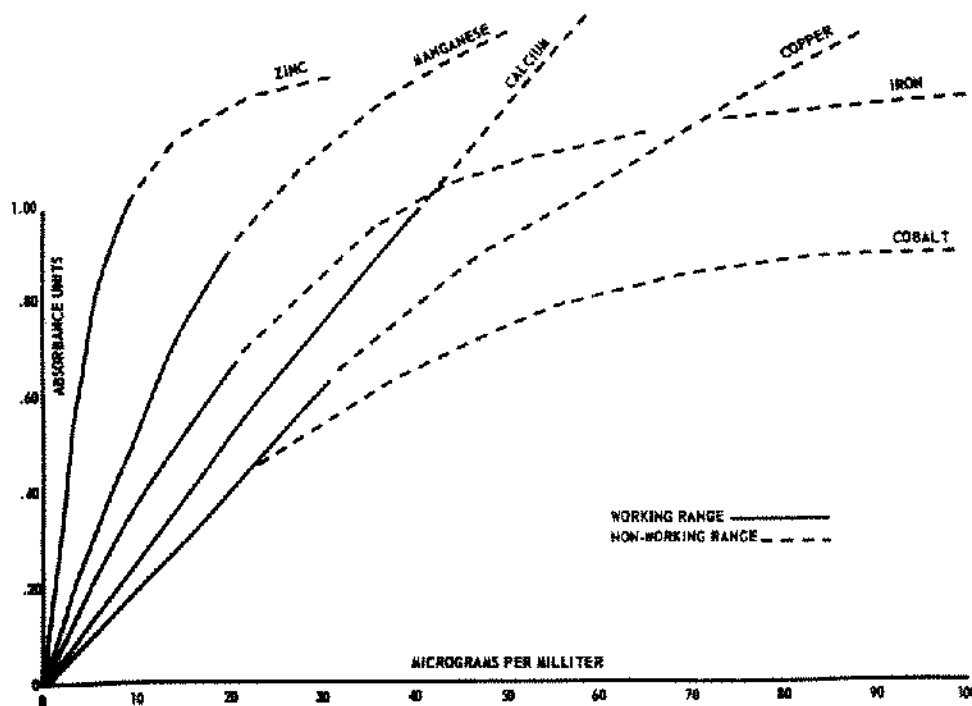


Figure 6. Working Curves.

centrated solutions, but appears in many cases to be at least several weeks. However, working range standards may easily be made up on the day of their use.

Interferences

The analysis of agricultural salt products by AAS is complicated by interferences which may be classified mainly as matrix effects. A relatively concentrated salt solution causes plugging of nebulizers, clogging of burner heads, low results due to differences between sample and standard solution viscosities and surface tensions, and light scattering in the flame. We have chosen to deal with these problems by using dilute sample solutions. In so doing, we avoid the clogging of nebulizer capillaries and burner heads, and reduce the differences between sample and standard solutions. No interelement interferences between the six metals of interest have been noted. (Slavin, 1968, pages 78-189, *passim*) An interference that may be expected is that of silica on manganese and iron. Such silica as may be present in the salt may reduce the apparent concentration of the two metals. However, calcium, which is commonly present in mineralized salt products, should control this effect. (Slavin, page 115) Moreover, there is some indication that this effect will be avoided when the 3-slot burner head is used. (Slavin, 1968, page 130)

Two interferences, principally effecting calcium determinations, may require additional sample treatment. Sulfate, phosphate, and silica, if present in the sample

solution, will form refractory compounds with calcium in the flame, and the apparent concentration of calcium in the sample will be reduced. This effect may be overcome by the addition of lanthanum to the sample, or if convenient, by analyzing for calcium with the nitrous oxide-acetylene flame. The other interference, sodium enhancement of calcium absorbances, is caused by the suppression of calcium ionization. Easily ionized elements, especially the alkali metals, supply electrons to the flame, and the equilibrium is shifted against calcium ionization. Addition of sodium or potassium to the standards will compensate for the presence of sodium in the sample. (Use of a fuel-rich, reducing flame, as described above, also enhances sample and standard absorbances, through the electron equilibrium in the flame or the lower temperature compared to that of a stoichiometric flame. (Slavin, 1968, page 91)) Matrix matching has been avoided in our procedure, but may become necessary in some calcium determinations. In that case, we may either match matrices of samples and the composite standards, or of samples and separate calcium standards only. Either way, it would involve addition of 1000 ug/ml sodium to the standards, and 1000 ug/ml lanthanum to both samples and standards. As noted previously, sample and standards have been matched in acid content.

Alternatives to dilution

We have dealt with the difficulties of salt matrices by resort to dilute sample solutions. The 3-slot burner head

can tolerate higher salt concentrations than we have chosen to use, though careful attention will have to be paid to the possibility of fluctuating solution uptake rates due to nebulizer capillary clogging. Sample and standard matrices will have to be matched when solids are at levels above one per cent, and perhaps at somewhat lower levels as well. (Slavin, 1968, pages 64, 72) When solutions of this sample concentration are analyzed, the concentration of the analyte may give absorbances lying beyond the useful portion of the working curve. However, the sensitivity of the determination may be reduced in several ways, and the useful analytical range correspondingly increased. Two such methods are to reduce the flame cell path length, and to use another, less sensitive spectral line. Changing the path length may easily be accomplished by rotating the burner head 90 degrees, so that the source radiation traverses only the width, and not the length, of the flame. Sensitivity reductions of 10–20 times may be expected for calcium. (Slavin, 1968, page 87) Preliminary results of tests in which standards were made up with 1.0% acid, 1.0% salt, and 0.1% lanthanum, indicate that the useable portion of the working curve is extended to between 100 and 500 ug/ml for all six metals.

The other method, use of a secondary line, appears to be useful for copper (223 nm) and iron (374 nm) up to 300–400 ug/ml, and for cobalt (304 nm) and manganese (403 nm) up to 100 ug/ml. The zinc secondary line (308 nm) is unuseable due to its extreme insensitivity. The calcium secondary line (240 nm) is of dubious utility, though it has been reported to be useable for concentrations up to 1000 ug/ml. (Slavin, 1968, pages 87–88) Lamp emission at this wavelength is too weak at the normal

operating current, and noise is excessive when the lamp is run at the maximum specified current (Figure 4).

We are currently considering the addition of a background corrector to our spectrophotometer. This modification is reportedly valuable in correcting for background absorption—molecular and flame absorption, and light scattering—below 250 nm, and especially when relatively concentrated solutions are being analyzed. Improvements in precision and accuracy may be expected, since several of the analytical wavelengths lie in the affected region of the spectrum. The background corrector should also make use of more concentrated salt solutions, and the two methods of handling them outlined above, more attractive.

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